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Evidence of strong acceptor peaks in ZnO thin films doped with phosphorus by plasma immersion ion implantation technique

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The photoluminescence of ZnO films implanted with phosphorus ions using plasma immersion ion implantation has been studied. The samples were rapid thermal annealed at 700–1000 °C. A dominant acceptor-bound exciton ($A^{\circ}X$) peak around 3.35 eV was observed for the sample annealed at 1000 °C with no evidence of donor bound exciton peak at 3.36 eV. Moreover, the free electron-to-acceptor peak at 3.31 eV and the donor-to-acceptor pair peak at 3.22 eV certify the presence of acceptors in the annealed samples. I–V performed on p-ZnO/n-Si heterojunction diode clearly exhibited a rectifying behavior with a threshold voltage of 3.3 V. The results have been stable even after 5 months. These results show a promising method for achieving stable p-type ZnO films.

1. Introduction

Extensive research is being carried out on ZnO as a potential material for the fabrication of optoelectronic devices like laser diodes (LDs) and light-emitting diodes (LEDs) in the ultraviolet region due to its wide bandgap (3.437 eV at 2 K) and a large excitonic binding energy of 60 meV at room temperature [1–4]. However, the bottleneck of ZnO-based devices is the creation of reliable and reproducible p-type films. This is because ZnO is an intrinsically n-type material due to defects such as oxygen vacancies and zinc interstitials [5,6]. Moreover, the low solubility of dopants and self compensating process on doping further aggravates the problem [7,8]. Many studies have been conducted across the globe with an intention to make p-type ZnO using group I and group V elements as the p-type dopants [9–16]. Doping in these cases was achieved using non-localized mechanisms, which is not desirable for device fabrication.

Ion implantation is a suitable technique for attaining selective and localized doping. Although researchers have successfully demonstrated p-type ZnO films using a conventional ion implantation (CII) technique, the reports are minimal [17–20]. In this work, phosphorus implantation has been performed using a plasma immersion ion implantation (PIII) technique instead of the conventional method to make p-type ZnO films.

The PIII technique is a relatively new technique compared to conventional implantation. In this method, the sample to be implanted (called the target) is directly immersed in a pool of plasma ions to be implanted. A negative pulse is applied on the target, which drives the electrons away from it and forms a positive sheath around the target. As a result, the electrons in the plasma are attracted to the target and become implanted. It is superior to the CII method since it is much simpler and cost-effective. Furthermore, uniformity is easily achieved since the plasma is uniformly distributed across the target. The charging effect on the target gets reduced, leading to fewer implantation-related defects compared to CII. However, the inability of mass separation may cause impurities within the plasma to become implanted along with the dopants. The formation of secondary electrons limits its efficiency, and in situ monitoring of the dose in PIII becomes difficult [21].

2. Experimental details

Undoped ZnO thin films were deposited using radio frequency (RF) magnetron sputtering on highly resistant < 1 0 0 > n-type silicon substrates. A high-purity ZnO target (99.999%) with a 5-inch diameter was used. The target-to-substrate distance was kept at 70 mm. The deposition was performed for 40 min in an Ar ambient of 7×10^{-1} Pa at room temperature. A base vacuum of 2×10^{-3} Pa was achieved prior to the deposition. A resultant thickness of 350 nm was achieved.

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The samples were subsequently subjected to phosphorus implantation using the PIII technique to obtain Sample A. A high-voltage negative pulse of −2 kV was applied to the target for 30 s. The negative pulse had an ON time of 10 μs and a RF frequency of 5 kHz. The chamber pressure of 10 Pa was achieved from phosphine (PH_3) gas during implantation, which was carried out using an RF plasma power of 900 W. Post-implantation, the samples were rapid thermal annealed at 700°, 800°, 900°, and 1000 °C in oxygen environment for 10 s to eradicate implanted related defects from the sample to obtain samples B, C, D, and E.

Scanning electron microscopy (SEM) imaging was performed using Raith 150TWO to analyze the surfaces of the obtained samples. Samples were sent to RTG Mikroanalyse GmBH for secondary ion mass spectroscopy (SIMS) measurement for studying the depth profile of the implanted P ions. Temperature-dependent photoluminescence (PL) studies were performed to study the optical properties of the implanted films. A He–Cd laser with a wavelength of 325 nm was used for the purpose and a Si-detector array was used to capture the spectrum.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows representative SEM images of as-deposited sample, samples A and E. The presence of defects due to phosphorus implantation in sample A can be clearly observed. With an increase in annealing temperature, grains grow, and large grains in the films are clearly visible for Sample E, implying the removal of any implantation-related defects.

3.2. Optical properties

Low-temperature PL (8 K) spectra of various samples are shown in Fig. 2(a). An expected donor-bound-exciton ($D^{\circ}X$) peak around 3.36 eV is observed for Sample A along with deep-level defect peaks centered on 2.5 eV corresponding to the Zn interstitials, oxygen vacancies and implantation-related defects [22,23]. For Sample B, the near band edge (NBE) emission almost disappears, while the deep-level defect peak becomes dominant, signifying the increased number of defects in the sample. Upon annealing temperature increase, the NBE emission again starts to dominate the PL spectra as seen in samples C, D, and E. However, a noteworthy change in the emissions is visible for the different samples. Whereas a free electron-to-acceptor (FA) peak around 3.32 eV is dominant in Sample C, the acceptor-bound exciton ($A^{\circ}X$) peak around 3.35 eV becomes dominant for samples D and E. This result clearly depicts a change in carrier type from n-type for samples A and B to p-type in samples C, D, and E due to P implantation [22–24]. Since the implanted samples are annealed at higher temperatures, the P ions receive sufficient thermal energy to occupy the oxygen vacancy positions in the ZnO lattice and form shallow acceptors, thus increasing the acceptor concentration and giving rise to p-type films. To further validate the importance of phosphorus implantation and subsequent annealing, PL measurements were performed on the as-deposited and annealed samples without implantation (Fig. 2(b)). The absence of any acceptor peaks in these samples proves that implantation of P ions leads to an increase in acceptors and thus p-type film formation. The presence of the FA peak around 3.32 eV in samples D and E and the donor-to-acceptor pair (DAP) peak around 3.25 eV for samples C, D, and E further confirm the increase in acceptors. Moreover, with regard to annealing the samples at higher temperatures, the defect peaks are also minimized, revealing reduced numbers of acceptor-, donor-, and implantation-related defects. This clearly illustrates that annealing the samples at higher temperatures improves film quality and changes carrier type.

To clearly visualize the effect of annealing on the P ions, a SIMS study was performed on the samples (Fig. 3). Increased P counts along the depth of the ZnO film can be clearly observed at higher temperatures. This finding further supports the PL and SEM

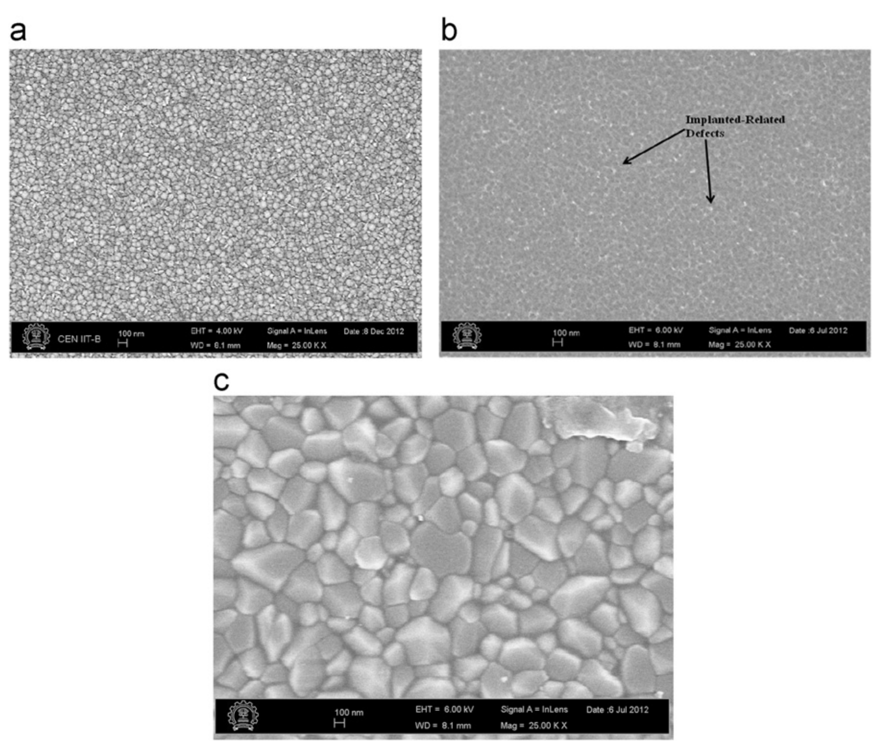

Fig. 1. Scanning electron microscopy images of various samples: (a) as-deposited sample, (b) Sample A; (c) Sample E. Reduced defects as well as grain formation can be clearly observed.